CHAPTER- 1

Introduction

1.1. General

Throughout the world with rapid growth of modern industry and the widespread use of fossil fuels has resulted in air pollution, which is increasing at an exponential rate over the last few decades. The combustion process of fossil fuels in power plants, automobiles and other incineration process are main source of air pollution. The exhaust gases from various stationary sources (Power plants, cement industries) and mobile engine contain mainly oxides of carbon (CO and CO_2), oxides of nitrogen (NO_x), hydrocarbons (HC), Sulphur dioxide (SO_2), particulates and soot. [1-3] Catalytic treatments are the most efficient technology to treat air pollutants and design of new, highly efficient catalysts is a key requirement for this technology. [4] The adverse impacts of these emissions on human health, climate and environment have forced legislation to control and limit such emissions. **Table 1.1** shows the sources and health effects of different pollutants emitted from stationary and mobile sources.

Among various air contaminants, nitrogen oxides (NO_x, including NO and NO_2) are notable major cause of air pollution. Released NO_x, can cause extremely serious environmental problems such as acid rain, ozone depletion and photochemical smog and it can affect global tropospheric chemistry. Notably, 90% of NO_x emission comes from combustion, including stationary and mobile sources. In fuel combustion from stationary sources, NO_x is primarily from coal fired power plants, electric power plant boilers. The NO_x emission from mobile sources is mainly from the exhaust gas of gasoline and diesel engines. [5]

Table 1.1. Sources of pollution emissions and their effects

Pollutants	Description	Sources	Health effects
Hydrocarbons (HC)	Organic compounds consisting entirely of hydrogen and carbon	Fuel molecules in the engine do not burn or burn only partially	Irritate the eyes, damage the lungs, and aggravate respiratory problems
Particulate matter (soot)	Impure carbon; very small particles of soot, dust, or other matter	Diesel engines, power plants, incomplete combustion of hydrocarbons	Eye irritation, asthma, bronchitis, lung damage, cancer, cardiovascular effects
Nitrogen oxide (NO_x)	Colourless gas Odourless Insoluble in water Toxic	Motor vehicles, electric utilities, and other industrial, commercial, and residential sources that burn fuels	Susceptibility to respiratory infections, irritation of the lungs and respiratory symptoms
Sulphur dioxide (SO_2)	Colourless gas with a sharp, irritating odour	Fossil fuel combustion at power plants, refineries, and other industrial facilities	Effects on the lungs; Wheezing, shortness of breath, chest tightness and other problems
Ozone (O_3)	Ozone is a bluish gas that has a pleasant odour	Emitted by cars, power plants, refineries, chemical plants, and chemically react in the presence of sunlight	Absorbs UV light, reducing human exposure to harmful UV radiation causes skin cancer and respiratory track effects
Carbon monoxide (CO)	Colourless, odourless, tasteless, flammable gas that is slightly less dense than air	Source of CO are cars, trucks and other vehicles or machinery that burn fossil fuels	High concentration of CO reduces the amount of O_2 that can be transported in the blood

	stream to critical organs like the heart and brain

According to a recent study, India's air pollution is primarily caused by steady coal burning in thermal power stations and a delay in implementing new technology. After automobiles, coal-based thermal power plants exhausted the second-highest amount of NO_x.[6] The different pollutants, their sources, and their contribution percentage is shown in **Fig. 1.1**.

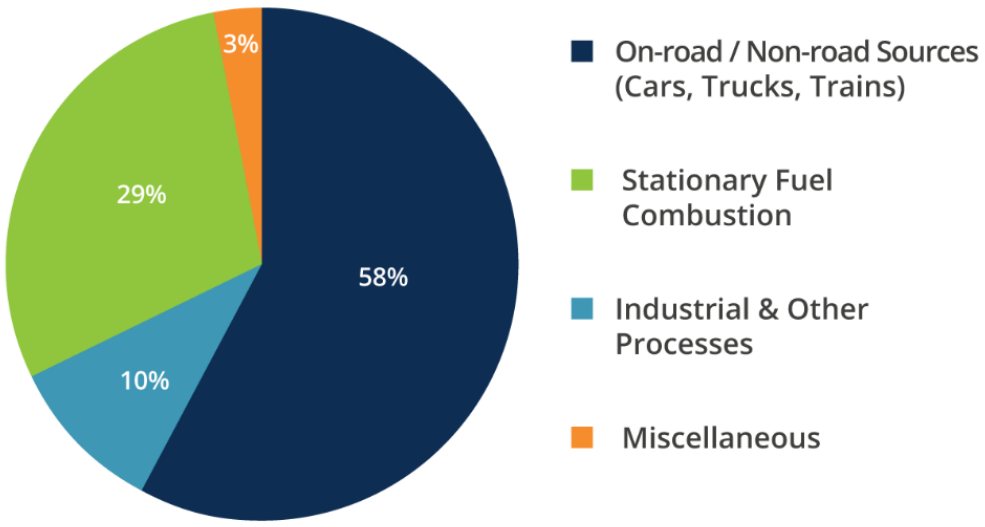

Fig. 1.1. NO_x emission sources of India

1.2. About NO_x

Seven compounds belong to the NO_x family. Since nitrogen dioxide (NO_2) is the most common form of NO_x in the atmosphere produced by anthropogenic (human) activity, NO_2 is the stand-in for this family of substances. Even in its unreacted state, NO_2 is a severe air pollutant that can lead to acid rain and ozone (O_3). It is significant to stress that the ozone we wish to reduce is tropospheric, or the ozone in the air we breathe daily. We are not talking about the toxic stratospheric ozone in the upper atmosphere, which is out of our reach. The stratosphere's ozone shields the troposphere and humans from the sun's ionizing radiation. The EPA has established National Ambient Air Quality Standards (NAAQS) for NO_2 and tropospheric ozone. The

NAAQS sets the minimum air quality standards required to safeguard the general public's health (primary standard) and welfare (secondary standard) from any known or anticipated negative impacts of pollution. The annual arithmetic mean concentration of NO_2 is 0.053 parts per million (ppm) (100 micrograms per cubic metre), which is the primary and secondary standard. [7,8,9]

About 80% of our air contains molecules of the comparatively harmless gas diatomic molecular nitrogen (N_2). Nevertheless, the chemical element nitrogen (N) can be reactive and have ionization levels (valence states) ranging from plus one to plus five as a single atom. As a result, nitrogen may form many kinds of oxides. The number of electrons that are either surplus (negative valence) or deficient (positive valence) in the ion compared to the neutral molecule determines the valence state using the Niels-Bohr atom model. **Table 1.2** listed the family of NO_x compounds and their characteristics.

Table 1.2. Family of nitrogen oxides (NO_x)

Name	Formula	Nitrogen Valence	Properties
Nitrous oxide	N_2O	1	Colourless gas water soluble
Nitric oxide	NO	2	Colourless gas slightly water soluble
Dinitrogen dioxide	N_2O_2		
Dinitrogen trioxide	N_2O_3	3	Black solid water soluble, decomposes in water
Nitrogen dioxide	NO_2	4	Red-brown gas very water soluble, decomposes in water
Dinitrogen tetroxide	N_2O_4		
Dinitrogen pentoxide	N_2O_5	5	White solid very water soluble, decomposes in water

The most common nitrogen oxides in the atmosphere are nitrous oxide (N_2O), NO, and NO_2. Biogenic sources like yeasts and plants produce large amounts of N_2O, often known as laughing gas. It is an analgesic that is only mildly reactive, meaning that, unlike an anesthetic, it does not make you feel any less pain. N_2O, an ozone-depleting chemical, interacts with O_3 in the stratosphere (above 50,000 feet) and the troposphere (below 10,000 feet), where it depletes ozone. N_2O has an extended half-life that ranges between 100 and 150 years. Any temperature can result in the oxidation of N_2O by O_3, which produces both molecular oxygen (O_2) and either NO or its dimer, dinitrogen dioxide (N_2O_2). In around two hours, the NO or N_2O_2 oxidizes fast to become NO_2. When an ionizing radiation photon from sunlight strikes the NO_2, it transforms into an ozone molecule from an oxygen (O_2) molecule. Nitric oxide (N_2O), like carbon dioxide (CO_2), is a "greenhouse gas" that traps heat emitted from the Earth and causes global warming. NO_x is the main form of NO that is emitted during combustion. According to the Zeldovich equations, NO forms in the air up to the oxygen limit (about 200,000 ppm) at temperatures higher than 1,300℃ (2,370°F). NO is generated in much lower concentrations or at temperatures lower than 760℃ (1,400°F). The ratio of air to fuel affects the amount of NO produced during combustion. When the mixture approaches the stoichiometric ratio (the ratio of chemicals entering the process) on the fuel-lean side, it becomes more perceptible. [10, 11] The Zeldovich equations are:

$$N_2 + O \text{--- } NO + N \qquad (1.1)$$

$$N + O_2 \text{ ---} NO + O \qquad (1.2)$$

$$N + OH \text{ ---} NO + H \qquad (1.3)$$

After the soils, lightning, and natural fires, maximum NO is exhausted by human activity (combustion from automobiles and industries). It is generally recognized that biological sources cause less than 10% of total NO emissions. NO is hardly soluble in water; only highly

sensitive people and infants are at risk. Both acid rain and the atmosphere contain NO_2. NO_2 changes into NO when it interacts with a photon to convert O_2 to O_3. Radicals from the photoreaction of VOC then oxidize this NO within hours to produce NO_2. Flue gas contains the compounds dinitrogen trioxide (N_2O_3) and dinitrogen tetroxide (N_2O_4) in extremely minute amounts. Due to their small part, their presence and impact on the atmosphere are ignored. The most highly ionized form of nitrogen oxide is dinitrogen pentoxide (N_2O_5). Due to its high reactivity, N_2O_5 breaks down in water to produce nitric acid (HNO_3). It is a good substitute for NO_x because NO is quickly converted to NO_2 and because N_2O is not very reactive, it lasts for a very long time. Others believe that NO and NO_2 should be classified as NO_x because of their involvement in ozone formation. Others think all nitrogen oxides, including N_2O, must be regulated. The most common types of NO_x, NO, and NO_2, are predominantly (but not completely) produced by anthropogenic activities. Since N_2O is mainly produced by living things, it is not regulated. Since NO_2 is the ozone precursor, it is sufficient to use its concentration as a stand-in for NO_x concentration for environmental purposes. [12,13]

1.2.1. Sources of NO_x

When fuel is burned at high temperatures, nitrogen oxides (a family of fatal, highly reactive gases) are generated. Most industries depend on combustion systems, such as engines and boilers, to produce heat or various forms of electricity to power their operations. Significantly, NO_x emissions from man-made fuel combustion systems vary in its intensity. The industries with the most NO_x emissions include transportation, electricity generation, industrial processing, and commercial and industrial heating. Mobile and stationary sources are the two primary sources of NO_x emission sources. [14] These are still some other sources from where NO_x is generated:

Natural sources

The severe heat from lightning, which is present in thunderstorms, causes the natural splitting of nitrogen molecules, which results in the formation of nitric oxide (NO). Due to precipitation with atmospheric water molecules, this nitric oxide may subsequently result in acid rain. A typical lightning flash under study in the mid-latitude subtropical thunderstorms transformed 7 kg of atmospheric nitrogen into chemically reactive NO_x. A total of 8.6 million tonnes of NO_x are released due to lightning each year, with 1.4 billion lightning flashes. However, it was found that most of the NO_x emissions come from fossil fuel combustion, estimated to be 285 million tonnes annually. [15]

Biogenic sources

Nitrogen fixation and agricultural fertilization have also increased the amount of NO_x in the atmosphere by stimulating microbial nitrogen fixation. [16]

Industrial /anthropogenic sources

Most industries depend on combustion systems, including automobiles and furnaces, to produce heat or electricity to power their operations. Every artificial fuel combustion system has different quantities of NO_x emissions. Examples of man-made sources are energy production, transportation, industrial processing, and heating for commercial and industrial applications. The several anthropogenic sources of NO_x can be categorized as seen in **Fig. 1.2**.

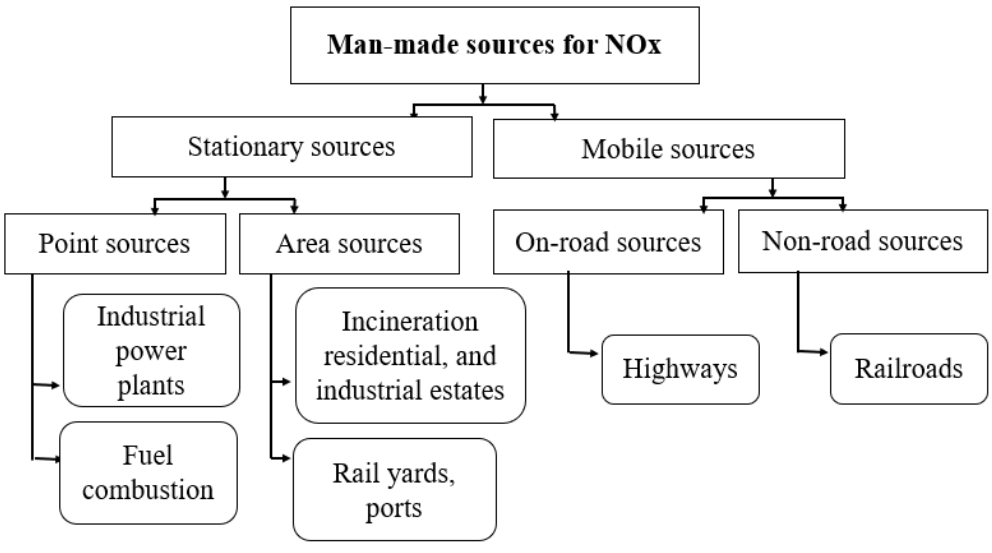

Fig. 1.2. Man-made sources of NO_x

Diesel and gasoline engine exhaust vary primarily in two ways. The diesel exhaust emits much more nitrogen oxides (NO_x) than gasoline exhaust. Second, the exhaust is much cleaner, containing much less carbon monoxide and a higher proportion of unburned hydrocarbons and carbon monoxide than the exhaust from a typical gasoline-powered vehicle.

1.2.2. Type of NO_x

Thermal NO_x

Thermal NO_x is the most prominent NO_x source due to combusting fuel at high temperatures. The NO_x emissions result from N_2 molecules being oxidised at high temperatures in the combustion air. When combustion air reaches a high temperature, usually 1600°C (2900°F), nitrogen and oxygen molecules dissociate into their atomic states and undergo reactions. There are three main reactions (the extended Zeldovich mechanism) that cause thermal NO_x (Reaction (1.1), (1.2), and (1.3)). Zeldovich gave the reactions and are the principal reactions that govern thermal NO_x formation. [17] All three reactions are reversible.

Fuel NO_x

Nitrogen cyclic compounds are present in fossil fuels, coal, and other hydrocarbons, producing this type of NO_x. The cyclic nitrogen compounds are less reactive than sulphur-based compounds, so removing them from combustion was challenging, resulting in NO_x production. The formation of NO_x occurs mainly by two methods. The initial one is the oxidation of volatile nitrogen species during the initial stages of combustion. Before oxidation, nitrogen and the volatiles mix to generate a sequence of intermediates that oxidize to NO. The second approach entails burning the nitrogen present in the char matrix as part of the combustion of the char component of the oils. The amount of nitrogen in the fuel, the rates of all surplus air, and the relative distribution of primary and secondary combustion air all affect the production of fuel NO_x. [18]

Prompt NO_x

The air nitrogen atom reacts with fuel radicals like C, CH, and CH_2 to produce immediate NO_x. The reaction chemistry cannot be explained like first two situations. In this combustion, nitrogen species, including CN (cyano radical), HCN (hydrogen cyanide), NH (nitrogen monohydride), and H_2CN (dihydrogen cyanide), which can be oxidised to NO. Prompt NO_x levels are very low in fuels made by nitrogen radicals. Prompt NO_x can be a significant source of NO_x in the low-temperature combustion of oxygenated fuels like biodiesel. [19]

1.2.3. Effect of NO_x on environment and human being

When NO_x reacts with moisture, ammonia eventually forms nitric acid vapour and related compounds. Humans and animals can suffer premature deaths due to microscopic vapours that can deeply penetrate their sensitive lung tissues. It is possible to develop respiratory illnesses such as bronchitis or emphysema after inhaling fine particles or to have existing heart and lung conditions aggravated by fine particles. In sunlight, NO_x reacts with VOCs (volatile organic compounds) to form ozone. The effects of ozone on humans can be numerous, causing severe lung damage in asthmatics. The impact of ozone on children and older people is also very severe. Also, ozone can be transported by the wind far from its source, causing adverse effects far from its source. In the United States, 50 percent of the population lived in areas not compliant with ozone standards. Several nitrate radicals and nitrosamines are formed when NO_x reacts with ozone and some of these causes DNA mutations. [20,21]

NO_x gases have a crucial role in generating fine particles (PM). The most polluted city in the world is Delhi, the capital of our nation, where it is estimated that 10,500 people per year pass away due to air pollution. This is due to the combination of high vehicle density, crop burning, and industry emissions contributed to the increase in fine Particulate Matter (PM) levels in Delhi's neighbouring states between 2013 and 2014. In Delhi, the highest level of $PM_{2.5}$, the most hazardous type of airborne particulate matter, was found. These steadily rising levels of

air pollution cause adverse effects, especially among Delhi's women and children, such as lung-related diseases, including lung cancer and asthma. In the winter months, the smog is significantly worse. Smog's thick density causes many transport problems, such as air and rail traffic disruptions because of the interruption of visibility. Due to increasing air pollution levels, Indian meteorologists have detected a noticeable decrease in the wintertime maximum temperature in Delhi since 1998. [22, 23]

NO_x emissions reduce the number of methane molecules in the atmosphere by forming OH radicals, reducing the influence of greenhouse gases and causing global cooling. The concentration of hydroxyl has increased because of considerable NO_x emissions from ships, according to the Organisation for Economic Co-operation and Development. Methane emissions can be decreased through a reaction with OH, but several unknowns are associated with the claim, as mentioned above. Much of the NO_x is intended to end up in the soil as beneficial nitrates or nitrites that growing plants can absorb. [24,25]

Acid rain: Acid rain is defined as rain or any other type of precipitation in the atmosphere that is unusually acidic, meaning it has a low pH and higher levels of hydrogen ions than usual. The acidity or alkalinity of a substance is measured using a pH (potential for hydrogen) scale, which ranges from 1 to 14. A value of 7 separates the neutral solution from it. "Acid rainwater" refers to water with a pH value lower than 5.65. When polluting chemicals like nitrogen oxides and sulphur oxides are emitted from factories, power plants, and automobiles into the environment, rainwater in the atmosphere reacts with them and produces acid rain. Acid rain causes many harmful effects on vegetation, freshwater, insects, and aquatic living species. [26] It harms buildings by causing paint to peel, corrosion in steel structures like bridges, weathering of statues, and damage to stone structures and buildings, as well as various negative impacts on human health. Acid rain causes the leaching of nutrients from the soil, making them unavailable to plants and crops cultivated there, which lowers their production. It is also found that the salts

and heavy metals in soil and rocks are easily dissolved by acid rain. Government protection has provided data on ancient sites like the Taj Mahal and Red Fort that have also been affected by acid rain. [27] Acid rain does not affect human health directly. The acid in the rainwater is very dilute and has adverse effects. However, the particulates that cause acid rain (SO_2 and NO_2) negatively affect human health. Increased amounts of these particulates contribute to heart and lung problems such as bronchitis and asthma. [28] The following reactions show the chemical reactions involved in the formation of acid rain from NO_x and the formation of nitrogen dioxide from nitrous oxide:

$$NO(g) + (½)O_2(g) \rightarrow NO_2(g) \qquad (1.4)$$

Nitric acid and nitrous acid are produced when nitrogen dioxide reacted with water.

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq) \qquad (1.5)$$

More nitric acid is produced due to the nitrous acid and oxygen reaction being catalysed by atmospheric substances.

$$2HNO_2(aq) + O_2(g) \rightarrow 2HNO_3(aq) \qquad (1.6)$$

Global warming: It has been noted that the earth's temperature has been steadily rising since the advent of industrialization. The greenhouse effect is a natural phenomenon that significantly affects the entire planet's climate. The natural greenhouse effect has been made worse by human activity, especially the combustion of fossil fuels. The most common greenhouse gases human activities produce are carbon dioxide, methane, nitrous oxide, and fluorinated gases. The concentration of greenhouse gases in the atmosphere has increased, which has increased the greenhouse effect. It is highly concerning that the atmospheric concentration of nitrous oxide (N_2O), a greenhouse gas that is 300 times more potent than carbon dioxide on an equimolar basis, is rising. [29,30]

Ground level ozone formation: The massive automobile population emits significant amounts of HC, CO, and NO_x into the atmosphere. A chemical reaction between HC and NO_x and sunlight form ground-level ozone When stagnant air masses hang over urban areas for a long time, pollutants are trapped. These pollutants react with sunlight, turning them into ozone at ground level. Ozone is found in vast amounts in smog. CO is toxic to people directly. The three precursors to ozone are NO_x, CO, and VOCs. Nitrogen oxides (NOx), carbon monoxide (CO), and volatile organic compounds (VOCs) react in the atmosphere in the presence of sunlight, particularly the UV spectrum, to produce most of the tropospheric ozone. [31]

The reaction starts with the oxidation of CO by the hydroxyl radical (OH). The unstable radical adduct (HOCO) quickly reacts with oxygen to produce the peroxy radical HO_2. Then the peroxy radicals and NO result in NO_2, which is afterward photolyzed by UV-A radiation to form atomic oxygen, reacting with molecular oxygen to produce ozone.

These ozone precursors are most frequently found in anthropogenic sources such as industrial pollutants, automobile exhaust, and chemical solvents. Ozone precursors are often found in urban areas, but because winds may carry NO_x hundreds of km, ozone can also develop in less populated areas.

Respiratory Problems: It is a gas made up of a single nitrogen and oxygen atom. It is a poisonous gas that causes lung disease, respiratory problems, nose and eye irritation, lung tissue damage, and breathing problems. Before 50 years ago, most cancer patients came from smoking areas. But now air pollution is one of the significant issues of cancer problems. Among them, NO_x directly or by ozone formation or $PM_{2.5}$ is an essential contributor to cancer. [32]

NO_x contributes to the destruction and construction of tropospheric ozone, resulting in acid rain and smog. Diesel engines and power plants also emit this harmful air pollutant. NO is a critical molecule that plays a role in various physiological and pathological processes in

mammals, both beneficial and harmful. Motor transportation is the anthropogenic source that contributes the most to atmospheric nitrogen oxide pollution.

1.3. The Indian emission standard

To regulate pollutants released by internal combustion engines, including motor vehicles, the Indian government introduced the BS or Bharat Stage emission standards. Bharat Stage emission standards followed the European (Euro) emission standards, with a five-year time lag from them. Thirty-three cities in India had the BS-IV fuel standard by March 2020. The rest of India was still using standard BS-III fuel.

India implemented vehicle emissions standards in 1991 and tightened them in 1996, forcing car manufacturers to add technology upgrades such as catalytic converters to reduce exhaust emissions. The country notified its first environmental fuel specifications in April 1996, followed by a second round in 2000.

In April 1999, the Centre government notified BS-I and BS-II standards for metros and the rest of the country, roughly equivalent to Euro I and Euro II standards. Following the Auto Fuel Policy 2003, BS-III standards were introduced in April 2005 for 13 major cities, while BS-II standards were applied to the rest. [33]

BS-III and BS-IV norms were introduced simultaneously in April 2010 for 13 major cities and the rest of the country, respectively. The auto fuel policy roadmap, BS¬V, and BS-VI norms were planned to implement from April 1, 2022, and April 1, 2024. But in November 2015, the Ministry of Road Transport issued a draft notification, advancing the implementation of BS¬V norms for new four-wheel vehicle models to April 1, 2019, and existing models to April 1, 2020. The corresponding dates for BS-VI norms were brought forward to April 1, 2021, and April 1, 2022, for new and existing vehicles. But the government later made a "unanimous decision to leapfrog to BS-VI directly from 01/04/2020", as Road Transport & Highways

Minister Nitin Gadkari announced, skipped the BS-V stage altogether. [34] The Bharath stage norms and the equivalent Euro norms are mentioned in **Table 1.3**.

Table 1.3. Bharath and euro emission standards

Standards	Reference	Year	Light duty(gm/Km)	Heavy duty(gm/kWh)
India 2000	Euro I	2000	-	8.0
BS-II	Euro II	2001	-	7.0
BS-III	Euro III	2005	0.5	5.0
BS-IV	Euro IV	2010	0.25	3.5
BS-VI	Euro VI	2020	0.06	0.5

BS-VI norms require fuel with less than 10 ppm of sulphur content compared to less than 50 ppm sulphur in the BS-IV standard. The current refineries will find it challenging to manufacture this fuel grade. The NO_x limit for passenger cars for BS-VI is 0.08 (gm/kWh), in comparison with 0.25(gm/kWh), which requires a 66% reduction. [34]

All limits are defined in mass per distance (gm/km for light-duty vehicles) or mass per energy (gm/kWh, heavy-duty engines). NO_x emissions can be reduced in three stages, i.e., pre-combustion, in-cylinder modifications, and after-treatment systems.

1.4. Different techniques for NO_x removal

Various methods have been tried to reduce emissions, including engine tuning, alternative fuels, and exhaust gas after combustion. In addition to benefitting most emissions, these initiatives could also increase other harmful emissions. NO_x control technologies are classified into three categories: "Pre-combustion," "Combustion modification," and "Post-combustion Techniques." They include using low nitrogen fuels, altering the design, operating aspects of the combustion unit, and flue gas treatment after combustion. NO_x emissions can be reduced

using a variety of approaches. The most extensively utilized strategies for reducing vehicle NO_x emissions are combustion modification and selective catalytic reduction (SCR). However, NO_x reduction in combustion modification approaches is frequently limited, and SCR systems can be expensive. Other novel technologies, such as non-thermal plasma and pressure swing adsorption, are efficient and cost-effective for removing higher NO_x concentrations. However, they are still prohibitively expensive for treating large flue gases. As a result, ecologically acceptable and cost-effective options for comprehensive NO_x exhaust treatment are required. [35,36]

1.4.1. Pre-treatment

As reported fuel, NO_x is not significant due to the presence of a high-temperature combustion zone in the presence of air, leading to NO_x formation. However, removing nitro-cyclic compounds from the fuel is difficult due to less reactivity.

1.4.2. Combustion modification

Automobiles are the primary source of high air contaminants. The amount of pollutants a vehicle emits is determined by many factors, including the engine's design and operation. This technique alters combustion conditions by changing the air-to-fuel ratio, designing a low NO_x burner, or by exhaust gas recirculation (EGR). Amon these, EGR is the most economically feasible and currently used technique for NO_x control. It is achieved by supplying a mixture of air with exhaust gas, decreasing the combustion temperature, and thus reducing the NO_x formation. [37]

Exhaust gas recirculation (EGR) is an ancient practice initially designed for spark-ignited engines but is now used to manage diesel emissions. Many engines manufactured after 1973 contain an EGR valve between the exhaust and intake manifolds. Its only goal is to reduce NO_x emissions by implementing a metered and limited pollution reduction scheme, increasing inert

gas in the air/fuel combination, and lowering peak combustion temperature ranges. EGR systems are divided into high-pressure EGR systems and low-pressure EGR systems. In high-pressure systems, a portion of the exhaust gas upstream of the turbocharger is redirected to the intake manifold. The exhaust gas is collected from the exhaust pipe and introduced between the intake air filter and the turbo compressor in low-pressure EGR systems, usually after treatment. EGR systems help to reduce NO_x emissions in a variety of ways. The oxygen level of the combustion mixture is reduced by diluting the incoming air with combustion products and exhaust gas. Second, dilution and using heat absorbers like CO_2 and H_2O lower the peak combustion temperature.[38]

1.4.3. Post-treatment

To reduce uncontrollable NO_x emissions from fuel treatment or combustion phenomena. i.e., due to the limitation of EGR in controlling NO_x emission, after-treatment methods have been developed to achieve strict regulation standards. There are some post-treatment methods for NO_x reduction.

Two-way catalytic converters

A two-way catalytic converter can do two things simultaneously: convert CO to CO_2 and unburned hydrocarbons (unburned and partially burned fuel) to CO_2 and H_2O.

$$2CO + O_2 \rightarrow 2CO_2 \qquad (1.7)$$

$$2CaHb + (2a+b/2)\ O_2 \rightarrow 2aCO_2 + bH_2O \qquad (1.8)$$

This type of catalytic converter is extensively used in diesel engines to reduce hydrocarbon and carbon monoxide emissions. It is also utilized in spark-ignited gasoline engines. They are being replaced with three-way converters due to regulatory regulations demanding a reduction in NO_x emissions. [39]

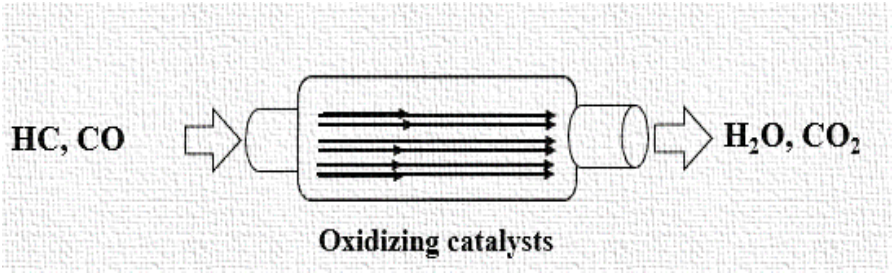

Fig. 1.3. Two-way catalysts

Three-way catalytic converter (TWC)

The three-way catalyst eliminates all three major exhaust contaminants at the same time by reactions between CO, HC, and NO_x. Three operations are performed simultaneously by a three-way catalytic converter (**Fig 1.4**).

In the first one, Nitrogen oxides are reduced to nitrogen and oxygen.

$$2NO_a \rightarrow aO_2 + N_2 \qquad (1.9)$$

In the second stage, Carbon monoxide is converted to carbon dioxide through oxidation.

$$2CO + O_2 \rightarrow 2CO_2 \qquad (1.10)$$

In the third stage, Carbon dioxide and water are produced by oxidizing unburned hydrocarbons.

$$2C_aH_b + (2a+b/2)\ O_2 \rightarrow 2aCO_2 + bH_2O \qquad (1.11)$$

These three reactions are most efficient when the catalytic converter receives exhaust from an engine operating slightly beyond the stoichiometric limit.

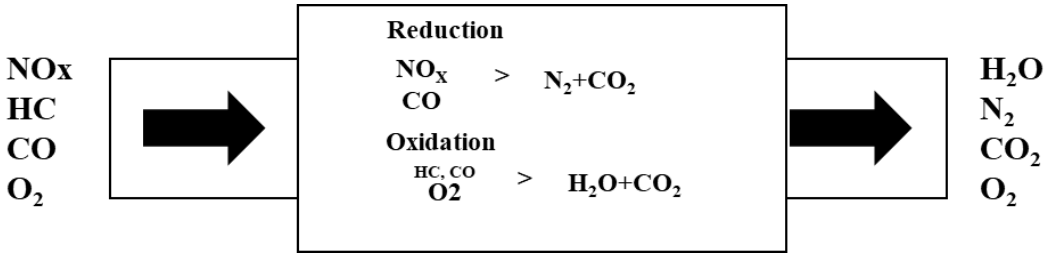

Fig 1.4. Three-way catalysts

Therefore, the converter will prefer two oxidizing reactions (CO and hydrocarbon oxidation) over the reducing reaction because it is running rich conditions. The reduction of NO_x takes precedence over CO and HC oxidation. Unfortunately, three-way catalytic converter technology is unsuitable with lean-burn engines, such as diesel-powered automobiles, which operate at high air/fuel proportions. While these engine technologies could be more fuel-efficient than stoichiometric gasoline engines, the three-way catalyst's failure to reduce NO_x emissions at high air/fuel fractions has limited their application in automobiles. [40]

Non-thermal plasma technique

For engines powered by diesel, the NTP technique can be used to reduce emissions. Exhaust gas NTP treatment is a promising NOx removal technology that works by injecting plasma into the exhaust gases. The fourth state of matter is plasma, with positive and negative charges that tend to stay electrically neutral over long distances. This substance comprises free electrons, ions, radicals, atoms, and molecules in various excitation states. When exposed to plasma, diesel and gasoline exhaust gases undergo chemical changes. In the presence of oxygen, oxidation processes can logically take precedence. The oxidation of hydrocarbons, carbon monoxide, and nitrogen oxides are examples of these reactions. [41,42]

Direct NO_x decomposition

The first happens in the absence of any reductant. Despite the favourable thermodynamics of direct NO_x decomposition, the reaction has significant activation energy instead.

$$NO \rightarrow 1/2N_2 + 1/2O_2 \ (H°_{298} \ -86.6 \text{ kJ/mol}) \qquad (1.12)$$

Cu-Zeolite is the most effective NO_x breakdown catalyst yet; however, its activity is low. Direct NO_x reduction at temperatures below 900°C, NO_x decomposition is thermodynamically

favourable. However, without the presence of a catalyst, the activation energy required for this reaction is too great. As a result, a catalyst is needed to lower the activation energy and hence speed up the reaction. Since no reducing agent is needed, this method is the simplest and most desirable. [43]

NO_x storage and reduction (NSR) or lean NO_x Trap

Nitrogen oxides (NO_x, including NO and NO_2) generated from lean-burn engines are rarely reduced in extra oxygen (TWC). One of the most promising methods for eliminating NO_x from lean-burn exhausts is the use of a lean NO_x trap (LNT). This reduces the amount of the exhaust after-treatment system significantly, particularly for diesel cars. A catalyst comprised of a storage component and a precious metal supported on Alumina is used in the LNT technique. There are two cycles to the reaction: a lean cycle and a rich cycle. NO is adsorbed onto the storage part in the lean cycle, oxidized to NO_2 over the catalyst, and then deposited as nitrate on the surface [44,45], shown in the **Fig. 1.5**.

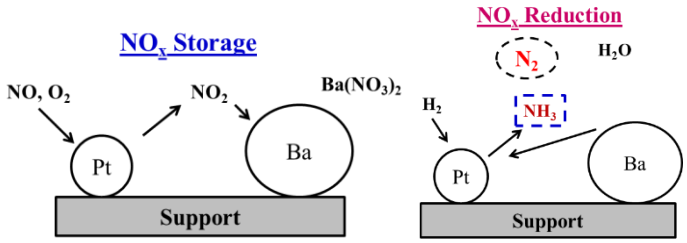

Fig. 1.5. NSR mechanism

This NO_x is liberated from the surface and reduced to N_2 by HC, CO, and H_2 produced by incomplete fuel combustion over a noble metal catalyst in the rich cycle. The final reaction is identical to SCR reactions, even though the reactions are carried out in two distinct processes. Sulphur poisoning is still a problem that causes the catalyst's deactivation. The ability of different SCR catalysts to form ammonia varies. At high temperatures, Pt/Al_2O_3 produces more NH_3, while temperatures change less influence Pd/Al_2O_3.[46]

Selective non catalytic reduction

Selective Non-Catalytic Reduction (SNCR) is a method adopted in power plants that burn coal, biomass, and waste to reduce nitrogen oxide emissions. The process involves injecting a reducing agent, typically ammonia or urea, into the firebox area of the boiler where the temperature of the flue gas is between 760°C and 1100°C where they react with Nitrogen oxide emissions (NO, NO_2) to reduce them into nitrogen (N_2), carbon dioxide (CO_2) and water (H_2O) Since it is safer to handle and store urea (NH_2CONH_2) than ammonia NH_3, urea (NH_2CONH_2) is preferred over ammonia NH_3. The reaction involving urea is shown below.

$$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (1.13)$$

The overall reduction reaction can be summarized below

$$4NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (1.14)$$

The reaction mechanism comprises NH_2 radicals that attach to NO and then decompose. The reaction requires an adequate time inside a specific temperature range, usually between 750°C and 1100°C. At lower temperatures and insufficient reaction time, the NO and ammonia do not react. The ammonia passes unreacted into the exhaust and is called Ammonia slip. This ammonia can react with other species in the flue gas and form ammonium salts. At temperatures above 1100°C Ammonia is oxidized into NO

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1.15)$$

In the above case, NO is formed rather than removed. Another disadvantage is mixing. Most of the NO will be formed in the centre and less near the walls, The reason being the walls are cooler than the centre. So, after injection, more ammonia must find its way to the centre and less near the wall vicinity. Otherwise, the NO in the centre will have insufficient ammonia for the reduction reaction. The surplus ammonia near walls escapes as ammonia slip. [47,48]

Even though Selective-catalytic reduction is shown to achieve 90% conversion efficiency, there are practical constraints of temperature, mixing, and reaction time that often led to poorer results. However, the absence of a catalyst in Selective Non-catalytic reduction can be considered more economical than selective catalytic reduction.

Selective catalytic reduction (SCR)

This technology is one of the most popular NO_x reduction technologies used to remove NO_x from stationary sources due to its high activity. has been in use since the 1970s for stationary applications, e.g., fossil fuel-powered power plants where it exhibited superior NO_x reduction. It was later implemented in gas turbine plants and marine applications in Japan and the USA. The first commercially feasible SCR system for European and Japanese heavy-duty applications was introduced in 2004.[49]

In this technique, NO_x (NO and NO_2) is converted with the aid of a catalyst into N_2 and H_2O. A gaseous reductant mainly anhydrous NH_3 or aqueous NH_3, H_2, hydrocarbons (HC) or CO is added to a stream of flue or exhaust gas and adsorbed onto a catalyst. It is important to note that the choice of reducing agent depends on specific requirements, application constraints, and regulatory standards. **Table 1.4** listed the advantages and disadvantages of various reductants. While NH_3 offers significant benefits, other reducing agents may be preferred in certain situations based on availability, infrastructure, and system compatibility.

Table 1.4. Different reducing agents used in SCR techniques

Reducing agents	Advantages	Disadvantages

Ammonia (NH_3)	-Reduces NO_x emissions at wide range of temperature 150-450℃ -Used extensively in stationary applications like power plants. -Relatively inexpensive and widely available	-Toxic in nature -Catalyst deactivation -An incomplete reaction cases ammonia slip problem. -It needs oxygen-rich conditions.
Hydrogen (H_2)	-Zero emission of greenhouse gas -No risk of ammonia slip -Can operate at low temperatures (below 300℃)	-It is mainly suitable for novel metal catalysts. -Highly flammable and poses safety risks.
Hydrocarbon (HC)	- Unburned hydrocarbons as reducing agents. - Can operate over a wide temperature range.	- Low de-NO_x performance and narrow temperature window compared to other de-NO_x systems (300–400°C).
Carbon monoxides (CO)	-Present in the vehicles exhaust - Used in the 260–400°C temperature range	- Less efficiency compared to others

The various advantages of using Ammonia (NH_3) over other reductants in selective catalytic reduction (SCR) systems are as follows:

a. High Reactivity: Ammonia reacts highly with nitrogen oxides (NO_x), thereby reducing NO_x emissions. It provides excellent conversion rates, resulting in high NO_x removal efficiency.
b. Wide Operating Temperature Range: Ammonia can operate effectively over a wide range of temperatures, from low to high. This flexibility allows SCR systems using ammonia as the reducing agent to maintain high NO_x reduction efficiency under varying operating conditions.
c. Established Technology: Ammonia-based SCR systems have been widely implemented and tested in various applications, such as power plants and large industrial facilities. The

technology and infrastructure for handling, storing, and injecting ammonia are well-established, making it a reliable option.

d. Cost-Effectiveness: Ammonia is relatively inexpensive compared to other reducing agents, such as hydrogen or formic acid. Its affordability makes it an attractive choice for large-scale applications with significant cost considerations.

e. Availability: Ammonia is readily available as a chemical compound and is produced in large quantities for various industrial applications. Its availability ensures a stable supply chain, reducing concerns about sourcing and distribution.

f. Storage Efficiency: Ammonia can be stored in a liquid state under moderate pressure, allowing for compact storage and more accessible transportation than gaseous reducing agents like hydrogen.

g. Lower Carbon Footprint: Compared to other reducing agents like hydrocarbons (e.g., diesel fuel), ammonia has a lower carbon footprint. Ammonia is carbon-free and does not contribute to carbon dioxide (CO_2) emissions during the SCR process. This environmental advantage aligns with sustainability goals and regulations to reduce greenhouse gas emissions.

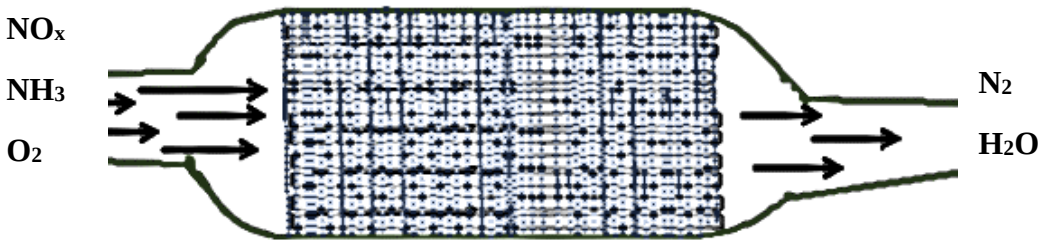

Fig. 1.6. Selective catalytic reduction system with NH_3 reductant

The major SCR reaction is

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1.16)$$

The above reaction is called a standard SCR reaction. It implies a 1:1 stoichiometric reaction between NH_3 and NO and the consumption of a small quantity of oxygen. The reaction without consumption of any oxygen shown below is much slower and is not relevant in the case of lean combustion gases

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (1.17)$$

While the reaction involving equimolar amounts of NO and NO_2 is much faster than the standard SCR reaction. This reaction is termed a fast SCR reaction

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \qquad (1.18)$$

Reactions with pure NO_2 are much slower It should be mentioned that the reaction with pure NO_2 is again slower than standard and fast SCR reactions.

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (1.19)$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \qquad (1.20)$$

Concerning the side reactions, some commonly used catalysts at high temperatures (above 400°C) to form nitrous oxide (N_2O)

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (1.21)$$

At temperatures higher than 500°C, the undesirable oxidizing properties of the SCR catalysts become more prominent as shown by in below reaction which represents the oxidation of NH_3 to NO, thus limiting the maximum NO_x conversion. [50,51]

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1.22)$$

At temperatures below 200°C in the NO_x feed containing NO_2, ammonium nitrate (NH_4NO_3) will be formed according to the below reaction

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \qquad (1.23)$$

1.5. Motivation

Frequent urbanization and increase in activity in transport industry led to the emission of various gaseous pollutants, such as sulphur oxides (SO_x) and nitrogen oxides (NO_x). Nitrogen oxides (NO and NO_2) are serious air pollutants as their emission can bring about many environmental problems, such as acid rain, greenhouse effects, photochemical smog and can also affect human health. Selective catalytic reduction (SCR) with NH_3 is currently a stablised technology for controlling the NO_x emission from stationary sources.

It is well known that catalyst plays a key role in the development of NH_3-SCR technology. Currently, V_2O_5-WO_3/TiO_2 or V_2O_5-MoO_3/TiO_2, which possesses high catalytic activity and SO_2 tolerance, is commonly used as the commercial catalyst for NH_3-SCR reaction in stationary sources. However, several disadvantages of the V_2O_5-based catalysts still exist for stationary sources:

- The poor low-temperature catalytic property (<300℃)
- The narrow reaction temperature window (300-450℃)
- Catalyst deactivation at high temperatures (>450 °C)
- The toxicity of V_2O_5

Despite the success of vanadium-based catalysts, their lack of efficiency at low temperatures has motivated researchers to develop more active catalysts at wide temperature ranges. Usually, the SCR catalyst is installed downstream of the desulfurized and electrostatic precipitator in power plants or industrial boilers; the exhaust temperature is lower than the working temperature window of the V_2O_5-WO_3(MoO_3)/TiO_2, so the catalyst must have good low-temperature activity and a wide temperature range. Therefore, there has been a strong interest in developing more active catalysts with wide working temperature windows, high N_2 selectivity, and low cost. Due to the appropriate reducibility and surface acidity of some

transition and rare earth metals (Cr, Mn, Fe, Co, Ni, Ce), they have been applied as active components for NH_3-SCR reaction. Among these, manganese oxides (MnO_x) have attracted great interest for application to low-temperature SCR catalysts as MnO_x has excellent redox ability at low temperature (100-450°C) and variable valence state, which plays a vital role in the NH_3-SCR reaction. However, pure MnO_x suffers from low thermal stability; therefore, supported manganese oxides have gained desirability for high thermal stability and better catalytic performance in SCR catalysts. Furthermore, catalysis systems based on MnO_x supported on various transition metal oxides (TiO_2, Al_2O_3, CeO_2, ZrO_2) have shown high performance for low-temperature SCR catalysts for NH_3-SCR reactions support must be catalyst support. Among the various oxides investigated as support, CeO_2 has attracted much attention as a supporting carrier due to its high oxygen mobility and unique redox properties, as cerium can rapidly switch between its two oxidation states (Ce^{3+} and Ce^{4+}).

1.6. Research Objectives

The global objective of this thesis is to synthesize and validate CeO_2-based catalysts for NO reduction via NH_3-SCR. Following are the specific objectives that will help achieve these targets:

- Study the effect of CeO_2 catalyst morphologies on the NO reduction
  - Synthesis of different ceria morphologies (nanorod, nanocube, nanopolyhedral) by hydrothermal method
  - Catalytic activity test for the NO reduction
- Study the MnO_x/CeO_2 catalysts for the low-temperature selective catalytic reduction of NO with NH_3
  - Synthesis of CeO_2-nanorod by hydrothermal method
  - Impregnation of MnO_x on CeO_2-nanorod by the wet-impregnation method
  - Catalytic activity test for the NO reduction

- Study the Effects of MnO_2 Crystal Phases in MnO_2/CeO_2 Catalyst for NO Reduction by NH_3-SCR
    - Synthesis of CeO_2-nanorod by hydrothermal method
    - Synthesis of different crystal phases of (α, β, γ and δ) MnO_2 by hydrothermal method
    - Impregnation of (α, β, γ and δ) MnO_2 on CeO_2-nanorod by the wet-impregnation method
    - Catalytic activity test for the NO reduction

1.7. Structure of the thesis

The thesis is structured in the following manner-

Chapter-2 deals with the current and previous research carried on using different type of catalytic in different reaction conditions based on NH_3-SCR technique.

Chapter-3 discusses the development of catalysts for NH_3-SCR and their characterization techniques. The different catalyst characterization tools, i.e., Nitrogen adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX), hydrogen-temperature-programmed reduction (H_2-TPR), and Raman spectroscopy are discussed in detail.

Chapter-4 deals with the synthesis and effect of different CeO_2 morphologies (nanorod, nanocube, polyhedral) on NO reduction morphologies.

Chapter-5 discusses the synthesis of different manganese oxides (MnO, MnO_2, and Mn_2O_3) supported on CeO_2-NR. The CeO_2-nanorod supports synthesized by the hydrothermal method. Further, the detailed characteristics and their catalytic performance for NO reduction using NH_3-SCR techniques have been discussed. The effects of different reaction parameters on the catalyst performance have also been discussed in detail.

Chapter-6 deals with the effect of different crystal phases (α, β, γ, δ) of MnO_2 supported on CeO_2-NR for NO removal. Furthermore, the structure performance relation of different catalysts was also explained.

Chapter-7 summarizes the main conclusions of this study and provides suggestions for future work.

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